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Susan B. Sinnott

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University of Florida - Gainesville
219 Grinter Hall
PO Box 115500
Gainesville, FL 32611 -5500

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14. ABSTRACT
We used classical molecular dynamics simulations to identify the nanometer-scale mechanisms by which a ceramic-based hybrid composite of PMMA and Al2O3 responds to mechanical deformation. The influence of factors such as the arrangement of the phases in lamellar and brick-and-mortar structures, atomic-scale roughness of the Al2O3 phases, and attachment of molecular grafts to the Al2O3 were explored. We also used first-principles, density functional theory calculations to examine the way in doping of yttrium aluminum garnet (YAG) influenced its optical properties. In particular, the identity of the dopants, their location within YAG unit cell, and their

15. SUBJECT TERMS
Hybrid ceramic-polymer materials, YAG, molecular dynamics simulations, density functional theory calculations, mechanical properties, optical properties

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Susan Sinnott
UU	UU	UU	UU		19b. TELEPHONE NUMBER 352-846-3778

Report Title

Role of Nanometer-Scale Mechanical Responses of Hybrid Ceramic-Based Materials on Toughening

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

"Investigation of Al2O3 Nanostructure Surfaces Using Charge Optimized Many Body Potentials", D. Yilmaz, T. Liang, S. Phillpot, S. Sinnott, AVS 59th International Symposium and Exhibition in Tampa, Florida, October 29-November 2, 2012.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Fellow of the Materials Research Society, 2012
Fellow of the American Physical Society, 2013

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Kai Yao	0.33	
Kamal Choudhary	0.66	
FTE Equivalent:	**0.99**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Dundar Yilmaz	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Susan Sinnott	0.14	
FTE Equivalent:	**0.14**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Kai Yao
Total Number: 1

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Summary of the most important results

In the case of the hybrid material project, the most important results include:

• Development of computational method to enable the building of hybrid polymer-ceramic structures without overlapping atoms.
• Optimization of charge optimized many-body potential for Al2O3 to enable reactive, atomic-scale modeling in simulations.
• Examined laminar and brick-and-mortar hybrid material structures subjected to compression and tension; documented atomic-scale responses and showed how the responses varied with the volume fraction of polymer.
• Introduced atomic-scale roughness and molecular grafts to the Al2O3 to see how these factors changed the mechanical responses. We have not yet been able to draw firm conclusions regarding their effects.

In the case of the doped YAG project, the most important results include:

• When Gd dopants are added, its f-electrons modify the optical properties of the YAG in the IR region. In contrast, Sc and Ga are not predicted to substantially modify the optical properties of YAG in the IR region.
• Doping with Gd, Sc, and Ga individually or in combination with one another is predicted to increases the opaque nature of the YAG in all cases, but less in the IR region than at higher wavelengths.

Technology Transfer

Final Progress Report

Role of Nanometer-Scale Mechanical Responses of Hybrid Ceramic-Based Materials on Toughening

Susan Sinnott

Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611-6400

Statement of the problem studied

We used classical molecular dynamics simulations to identify the nanometer-scale mechanisms by which a ceramic-based hybrid composite of PMMA and Al_2O_3 responds to mechanical deformation. The influence of factors such as the arrangement of the phases in lamellar and brick-and-mortar structures, atomic-scale roughness of the Al_2O_3 phases, and attachment of molecular grafts to the Al_2O_3 were explored.

We also used first-principles, density functional theory calculations to examine the way in doping of yttrium aluminum garnet (YAG) influenced its optical properties. In particular, the identity of the dopants, their location within YAG unit cell, and their concentrations were considered with guidance from experimental data from Lawrence Livermore National Laboratory.

Summary of the most important results

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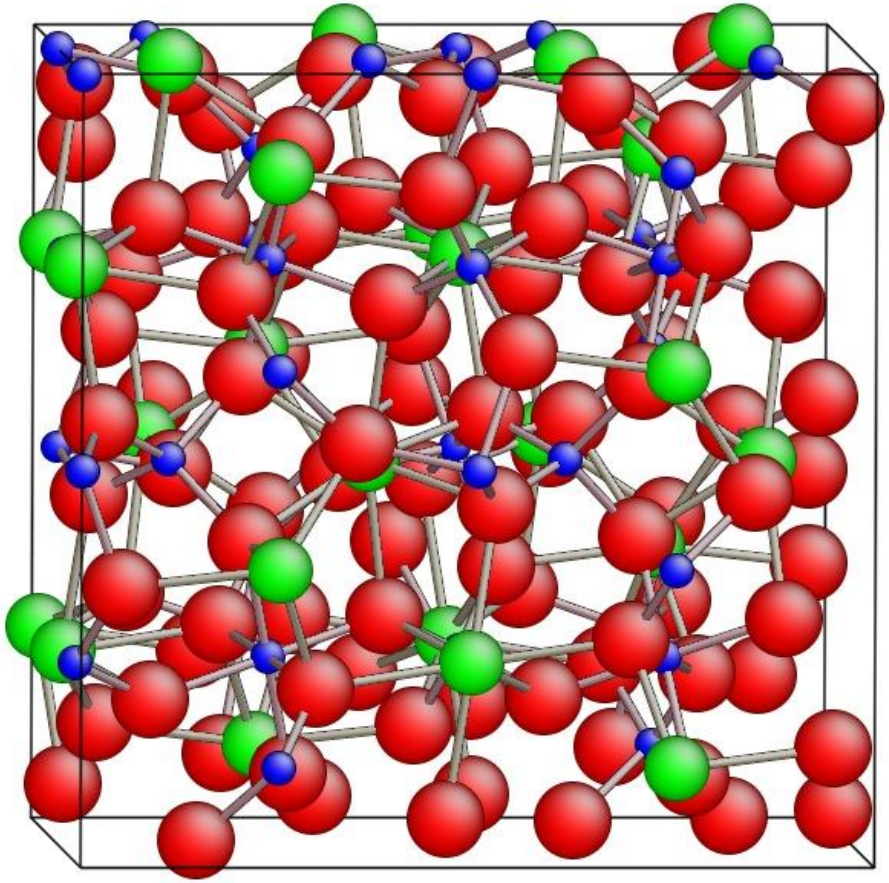
Role of Nanometer-Scale Mechanical Responses of Hybrid Ceramic-Based Materials on Toughening

Prof. Susan B. Sinnott
University of Florida

Final Report
July 6, 2014

Predicting Optical Properties of Doped YAG

Yttrium Aluminum Garnet

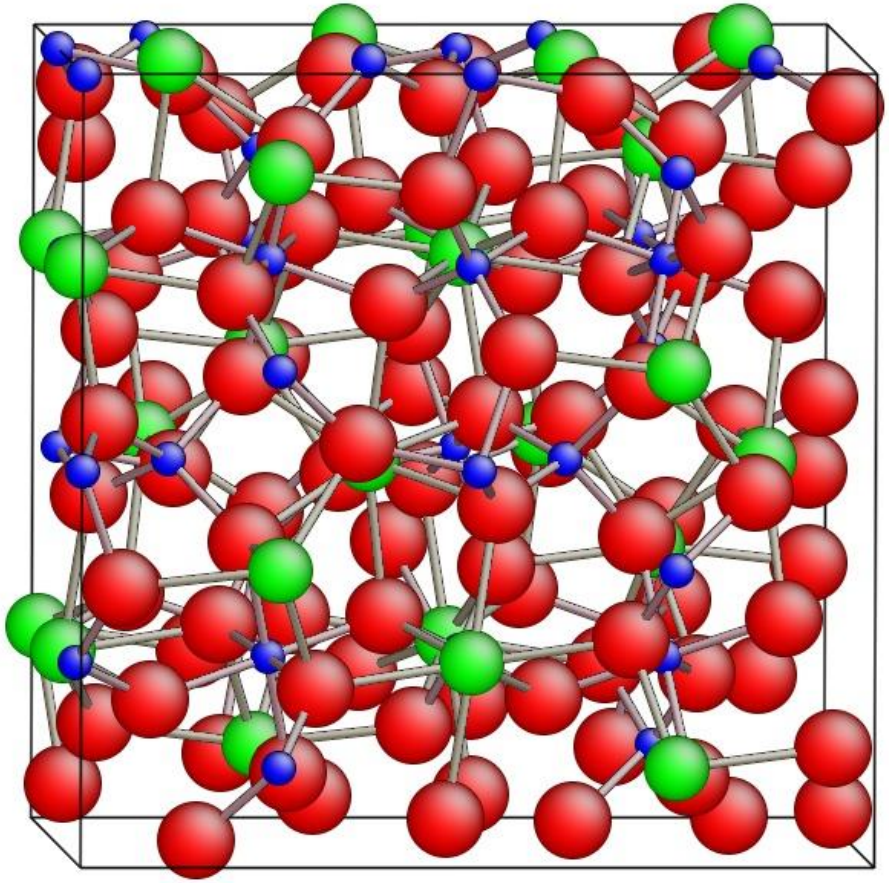


$Y_3Al_2Al_3O_{12}$ unit cell comprised of 160 atoms

- 24 Y—dodecahedral coordination
- 16 Al—octahedral coordination
- 24 Al—tetrahedral coordination
- 96 O

Structure with space group I*a*3*d*

Garnet Systems



Non-doped: YAG

- $Y_3Al_5O_{12}$

Gd-doped: GdYAG

- $(Gd_xY_{3-x})Al_5O_{12}$

x	% Gd
0.120	4
0.375	12.5
0.750	25
0.999	33.3
1.500	50
2.250	75
3.000	100

Computational Methods

Density functional theory using Vienna Ab initio Simulation Package (VASP)

- PBE pseudopotentials
- Single k-point (gamma) calculations
- Cut-off energy = 400 eV
- Energy convergence = 10^{-6} eV
- Force convergence = 10^{-2} eV/atom

Comparison with experiment

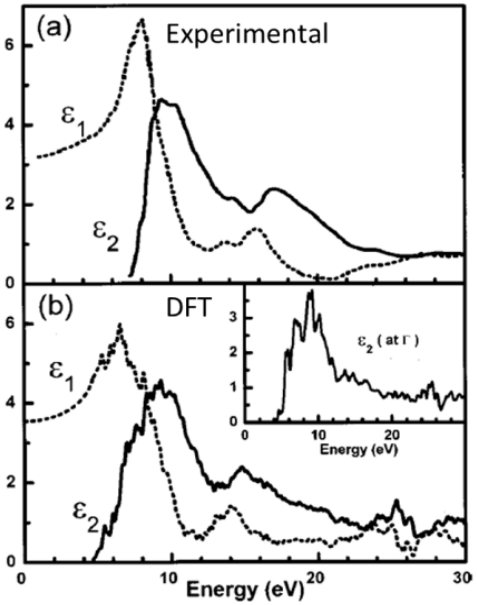
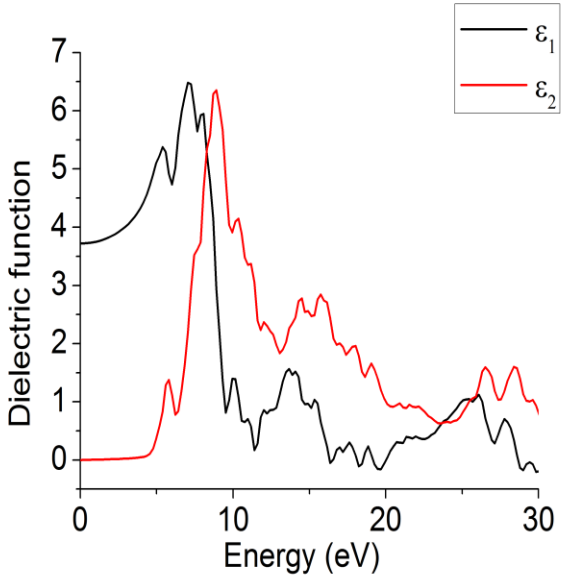


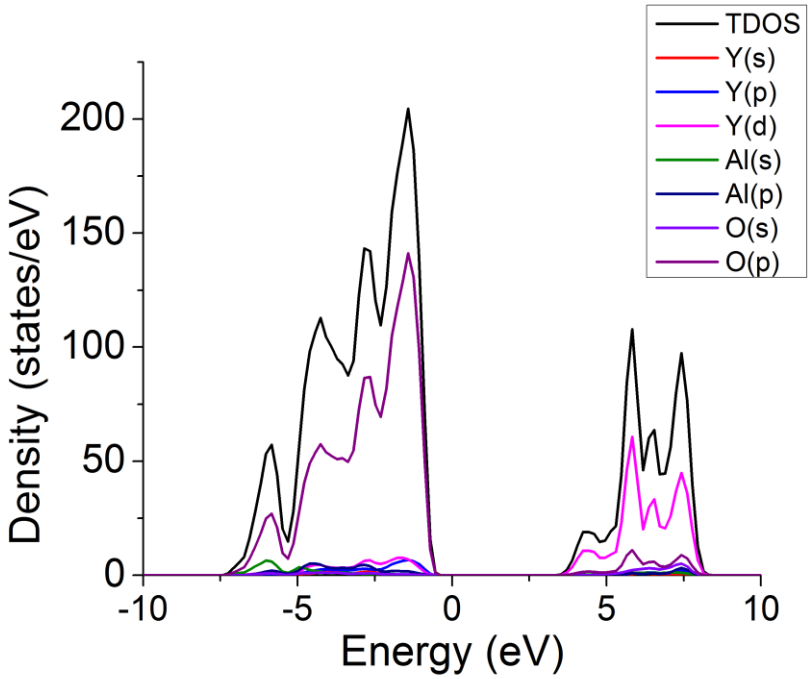
Fig. (a): $\varepsilon_1(0) \sim 3.40$
Fig. (b): $\varepsilon_1(0) \sim 3.54$



Above: $\varepsilon_1(0) \sim 3.72$

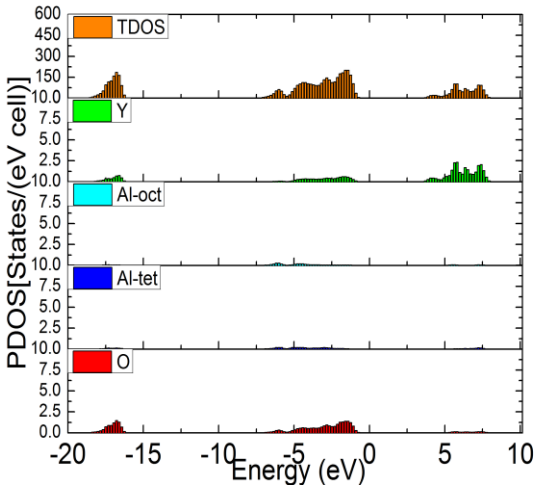
On left: Non-doped YAG, Xu, Y.N., Chen, Y., et al., Phys. Rev. B 65, 235105 (2002).
On right: Results from this work.

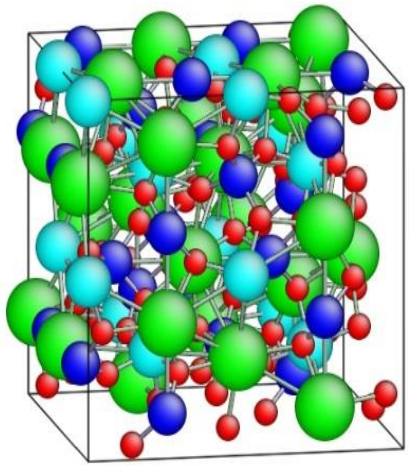
Electronic structure of pure YAG

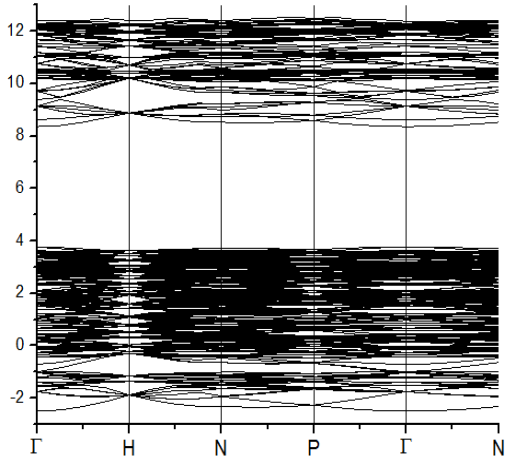


Light Comparison[3]			
Name	**Wavelength**	**Frequency (Hz)**	**Photon Energy (eV)**
Gamma ray	less than 0.01 nm	more than 10 EHZ	100 keV - 300+ GeV
X-Ray	0.01 nm to 10 nm	30 EHz - 30 PHZ	120 eV to 120 keV
Ultraviolet	10 nm - 390 nm	30 PHZ - 790 THz	3 eV to 124 eV
Visible	390 nm - 750 nm	790 THz - 405 THz	1.7 eV - 3.3 eV
Infrared	750 nm - 1 mm	405 THz - 300 GHz	1.24 meV - 1.7 eV
Microwave	1 mm - 1 meter	300 GHz - 300 MHz	1.24 μeV - 1.24 meV
Radio	1 mm - 100,000 km	300 GHz - 3 Hz	12.4 feV - 1.24 meV

DOS for YAG showing absence of any state in the infrared region

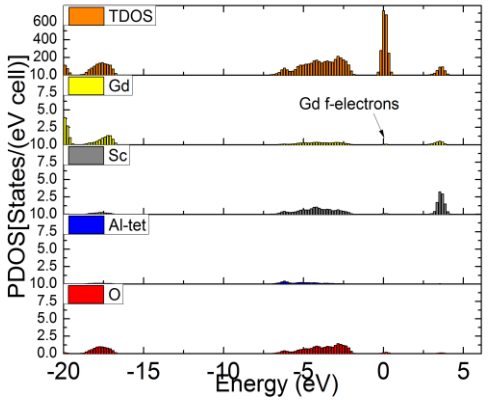


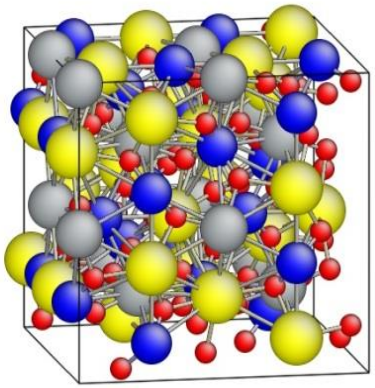


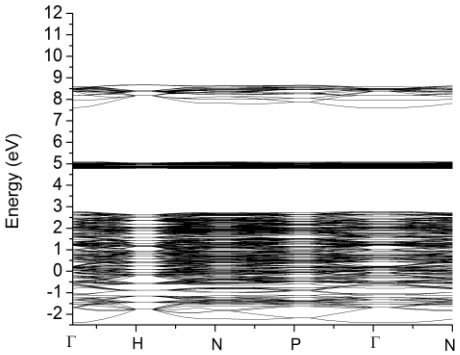


Partial density of states (PDOS), band-structure of pure YAG

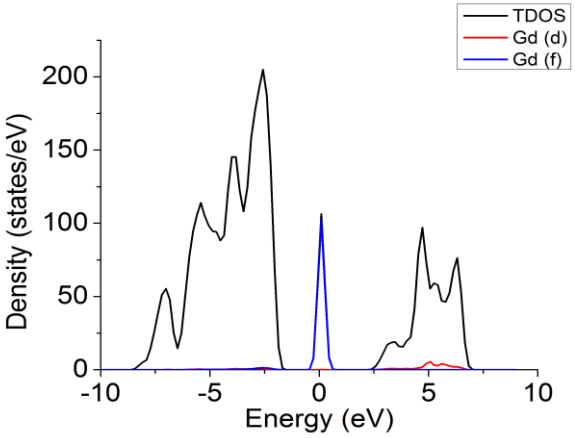
Introduction of Gd in YAG: Active in IR region





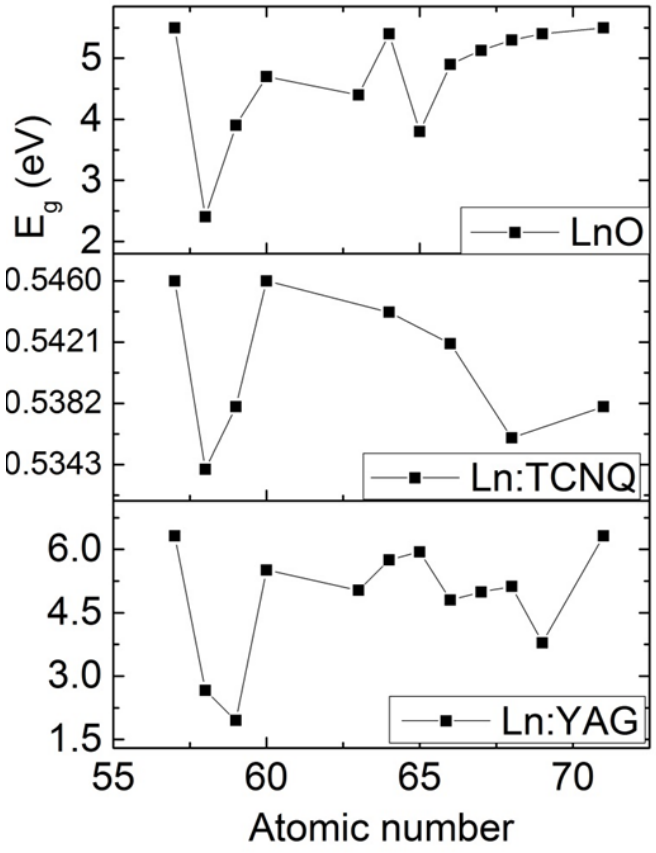


$Gd_3Sc_2Al_3O_{12}$:
Gd-f electrons are contributing extra energy states in the infrared region of YAG, may be responsible for infrared activity.



DOS for $(Gd_{0.375}Y_{2.625})Al_5O_{12}$

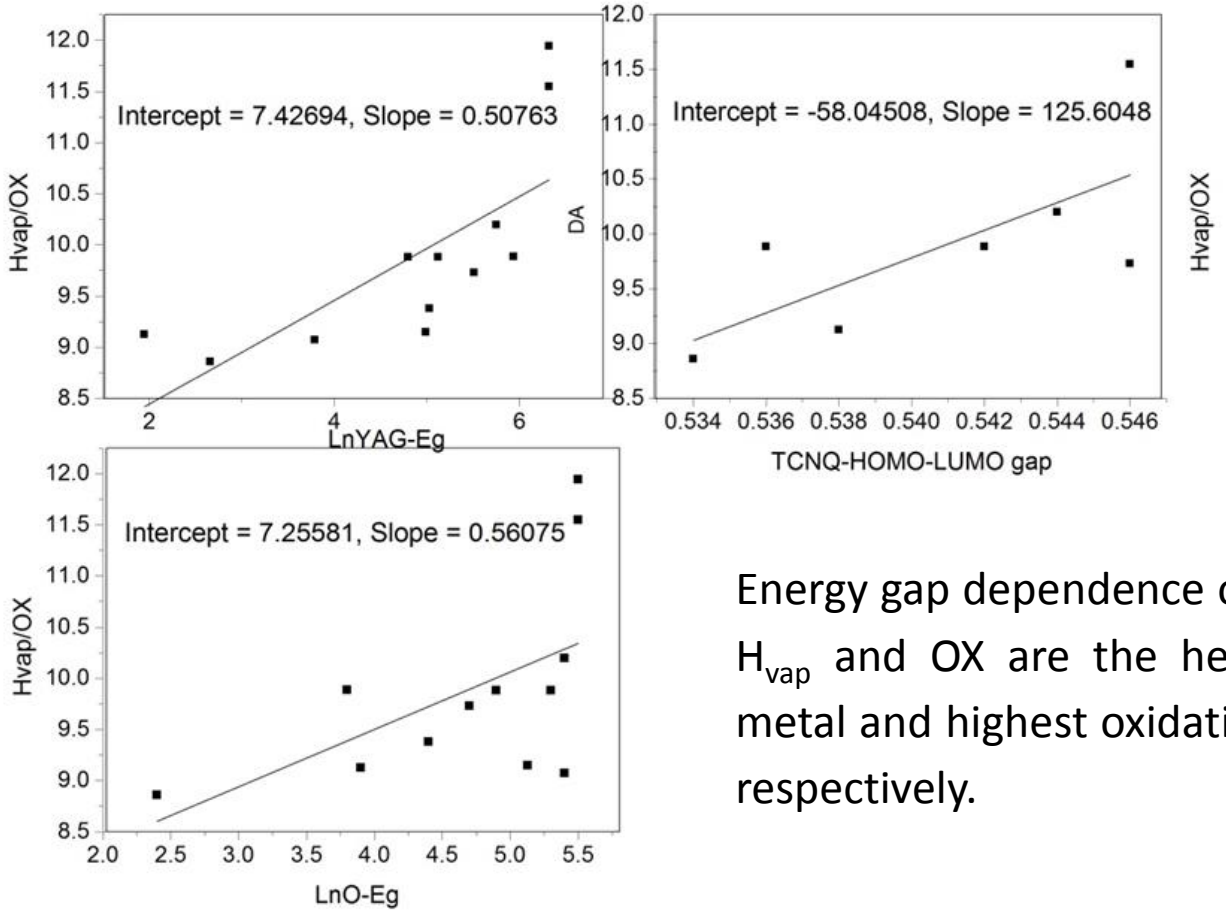
Relation between heat of vaporization and energy gap of lanthanide based organic and inorganic compounds



- Energy gap of lanthanide doped YAG, lanthanide-TCNQ (= 7, 7, 8, 8-tetracyano-p-quinodimethane) [1] complexes and lanthanide oxides.
- HOMO-LUMO gaps for all the lanthanides TCNQ complexes were not available.
- Energy and HOMO-LUMO gaps follow specific patterns.

[1] Zhang et al., Systematic study on electrochemical properties of a series of TCNQ lanthanide complexes, Journal of Organometallic Chemistry 695 (2010) 1493–1498.

Relation between heat of vaporization and energy gap of lanthanide based organic and inorganic compounds



Energy gap dependence on H_{vap}/OX, OX, where H_{vap} and OX are the heat of vaporization of metal and highest oxidation state of the metal, respectively.

Predicting Mechanical Properties of Al_2O_3-PMMA Hybrid Materials

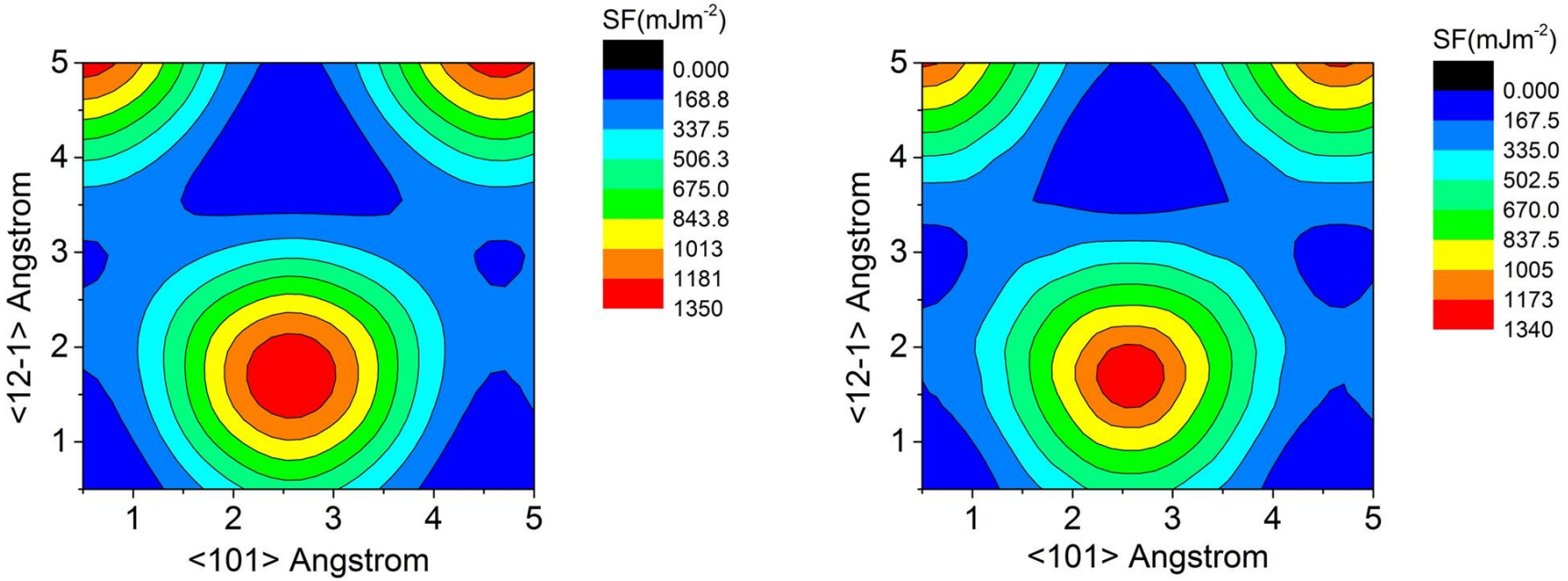
Objectives

- Use classical molecular dynamics simulations to elucidate the mechanical responses of PMMA-Al_2O_3 hybrid structures
- Determine how the laminar and brick-and-mortar structures compare to one another
- Understand the effects of degree of polymerization of the PMMA on the mechanical properties of the hybrid material.

Computational approach

- Classical molecular dynamics simulations
- Atomistic treatment
- Forces on the atoms calculated with the third-generation charge optimized many-body potential
- Focus on mechanical properties of Al_2O_3-PMMA hybrid materials as a function of hybrid structure, PMMA chain length, and system size
- Currently running: influence of surface roughness

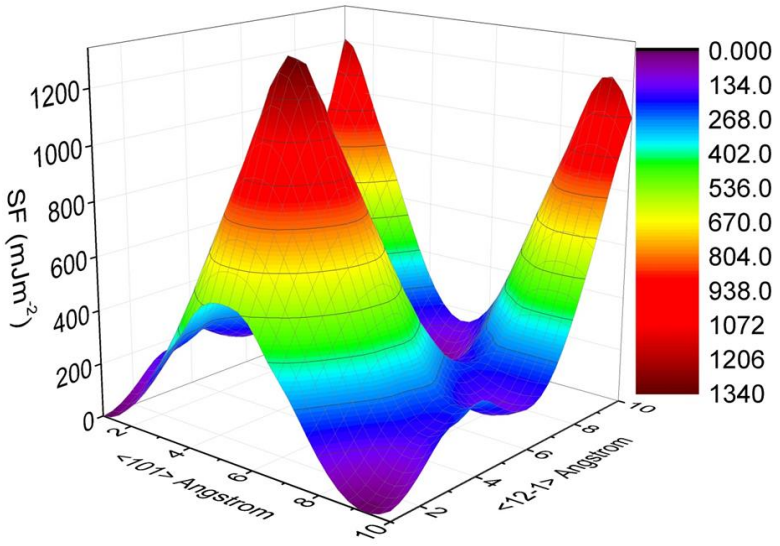
Stacking fault energy predicted for Al

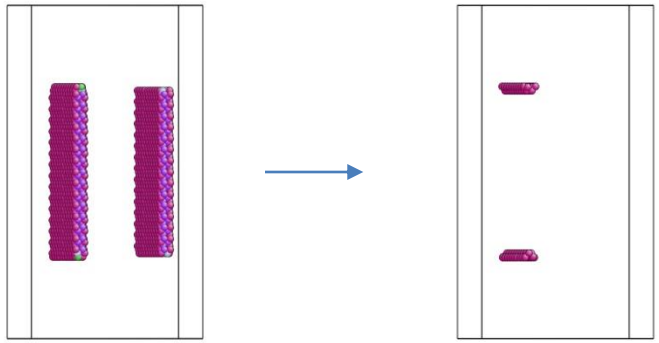


Stacking fault map predicted for Al using (left) the embedded atom method (EAM) potential and (right) the charge optimized many-body (COMB) potential.

The symmetry in the contours represents the periodicity in the system.

Stacking fault and dislocation splitting behavior of Al

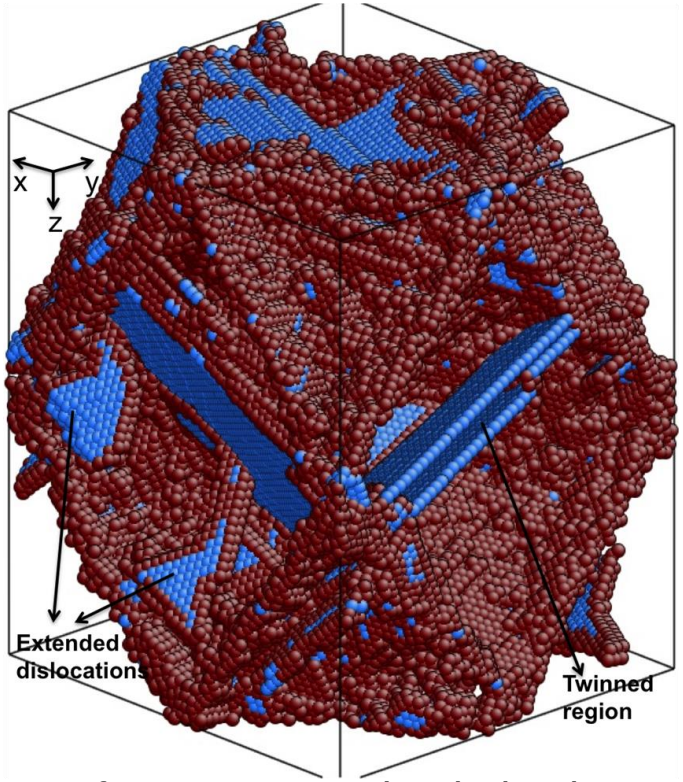




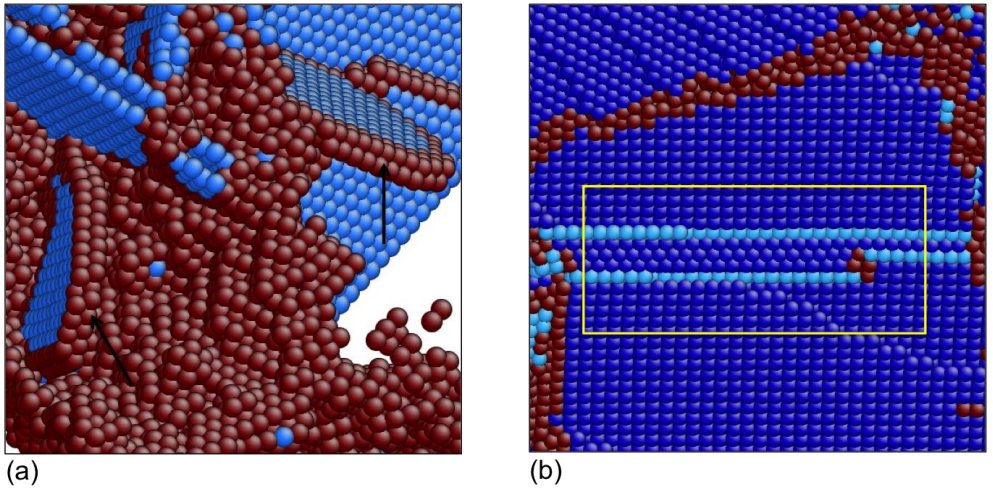
Stacking fault 3D-map using COMB that successfully predicts the $\langle 12\bar{1} \rangle$ direction would be preferred over $\langle 101 \rangle$ for dislocation propagation.

Dislocation splitting of an edge dislocation within a (111) plane of bulk Al is illustrated.

Mechanical deformation of polycrystalline Al predicted in MD simulations with COMB potentials



Left: A 13.8% strained Al polycrystal following constant strain. Red atoms represent disordered atoms (non-12 coordinates), light blue atoms are in an hcp environment. Atoms in an fcc environment are not shown for clarity.

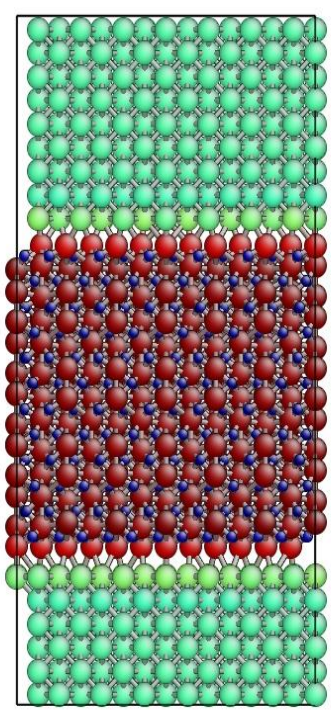


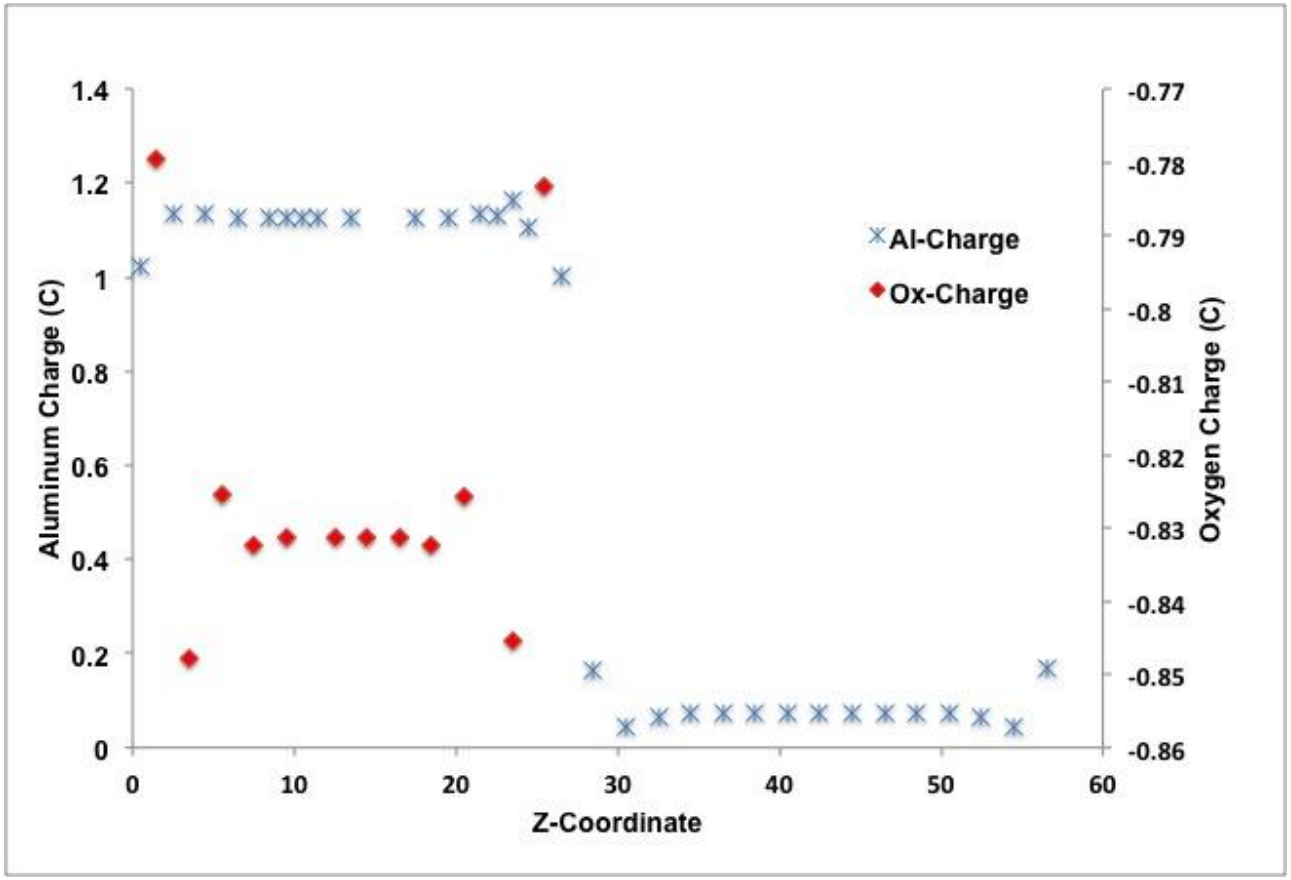
(a) Extended dislocations within the (111) plane are indicated by the black arrows.
(b) The yellow square highlights twinned region.

COMB predictions for Al_2O_3

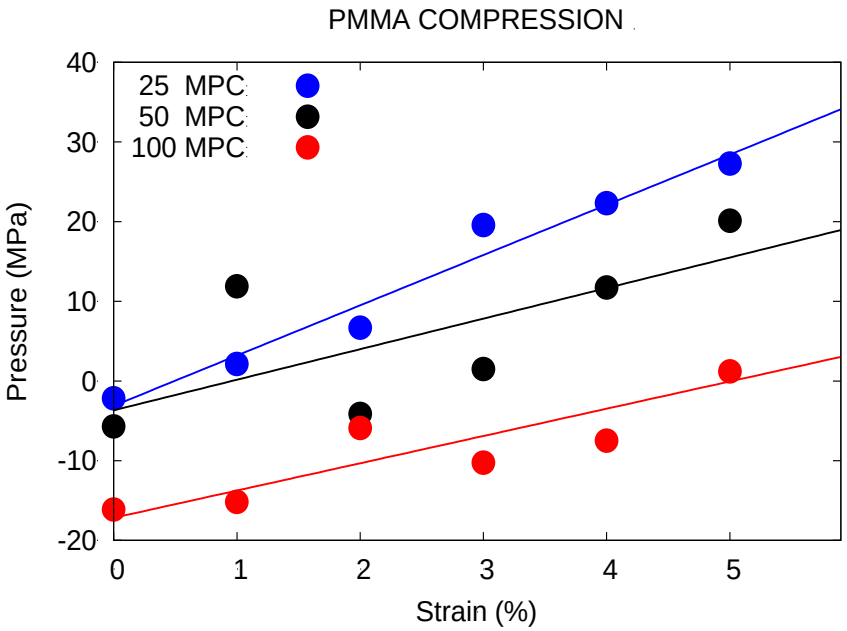
Structure	(Exp.,DFT)	COMB3	ReaxFF	ES+	Vashisth et al
H_f, Al_2O_3-Alpha (eV)	−17.3400	−17.235	-23.54	-17.34	-17.29
H_f,Al_2O_3-Bixb. (eV)	−16.3700	−15.33	-22.88		
H_f, Al_2O_3-Theta (eV)	−16.9600	−12.66	-23.35		
Hf, AlO-NaCl (eV)	-5.76	-5.65			
Hf, AlO_2-CaF_2 (eV)	-9.89	-9.09			
Al-interstitial (eV)	16.8000	2.41			
O-inerstitial (eV)	8.8400	10.13			
Val (eV)	8.4400	1.32			
VO (eV)	6.0900	13.8			
0001 Surface (J/m^2)	1.59	1.5	1.0	2.67	
Bulk Mod.s (Gpa)	254, 290	283	248	250	253
Shear Mod. (Gpa)	156, 172	160			
C11	497	505	537		523
C12	164	168	180		147
C13	111	163	106		129
C14	-24	0.0	-30		7.5
C33	498	545	509		427
C44	147	152	130		135
C66	168	146	179		174

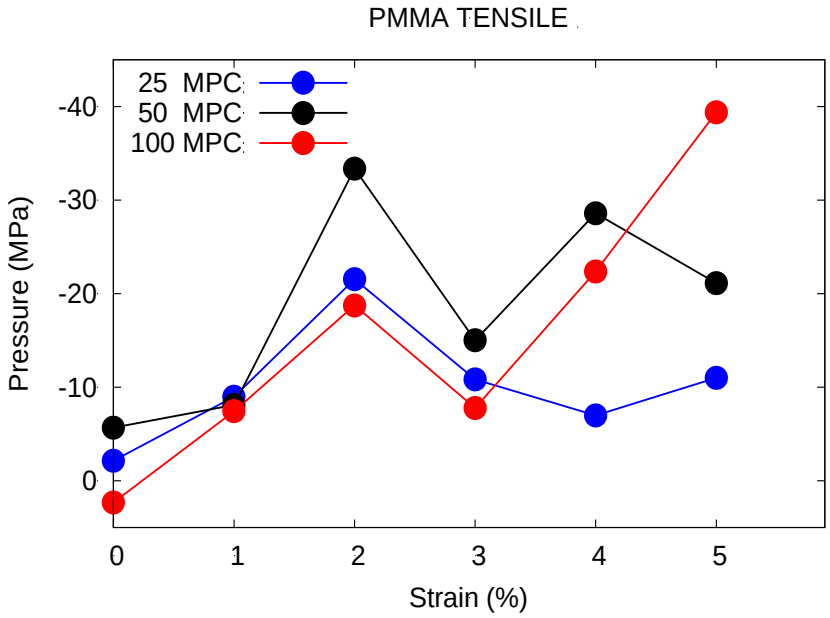
Predicted charge-spilling across the $Al_2O_3(0001)/Al(100)$ interface





Uniaxial compression and tension tests of pure PMMA





- Effect of chain length investigated
- Response to the compression depends on chain length
- Response to tension highly non-linear

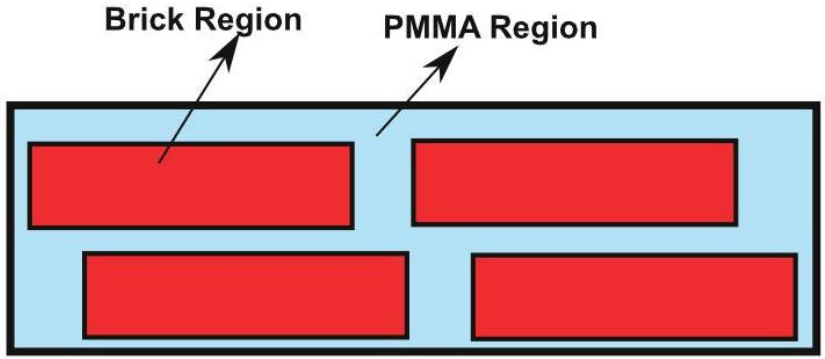
In-situ brick-and-mortar building

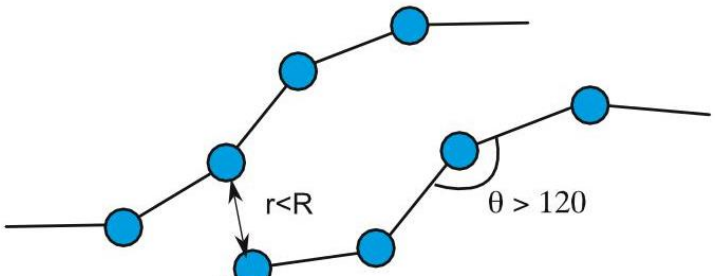
Brick and mortar building starts with defining regions of alumina (bricks) and PMMA (mortar) in the simulation box.

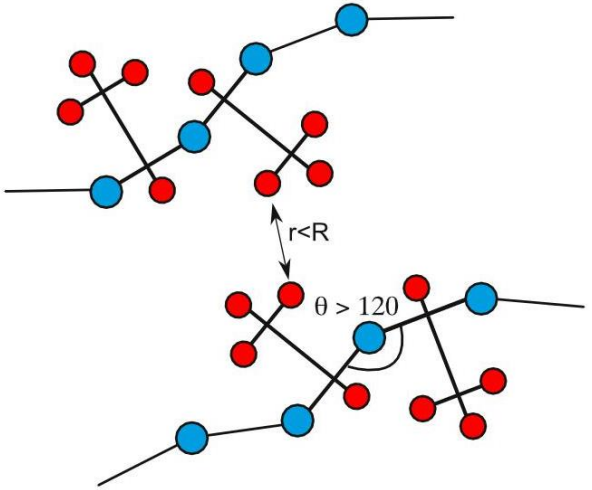
First PMMA chains are built using three constraints:

- Angle between two segments of chain should be greater than 120°.
- Distance between any beads should be greater than approximate size of the monomer (~0.5 nm).
- Distance between any PMMA atom should be larger than 0.08 nm to prevent over-coordination

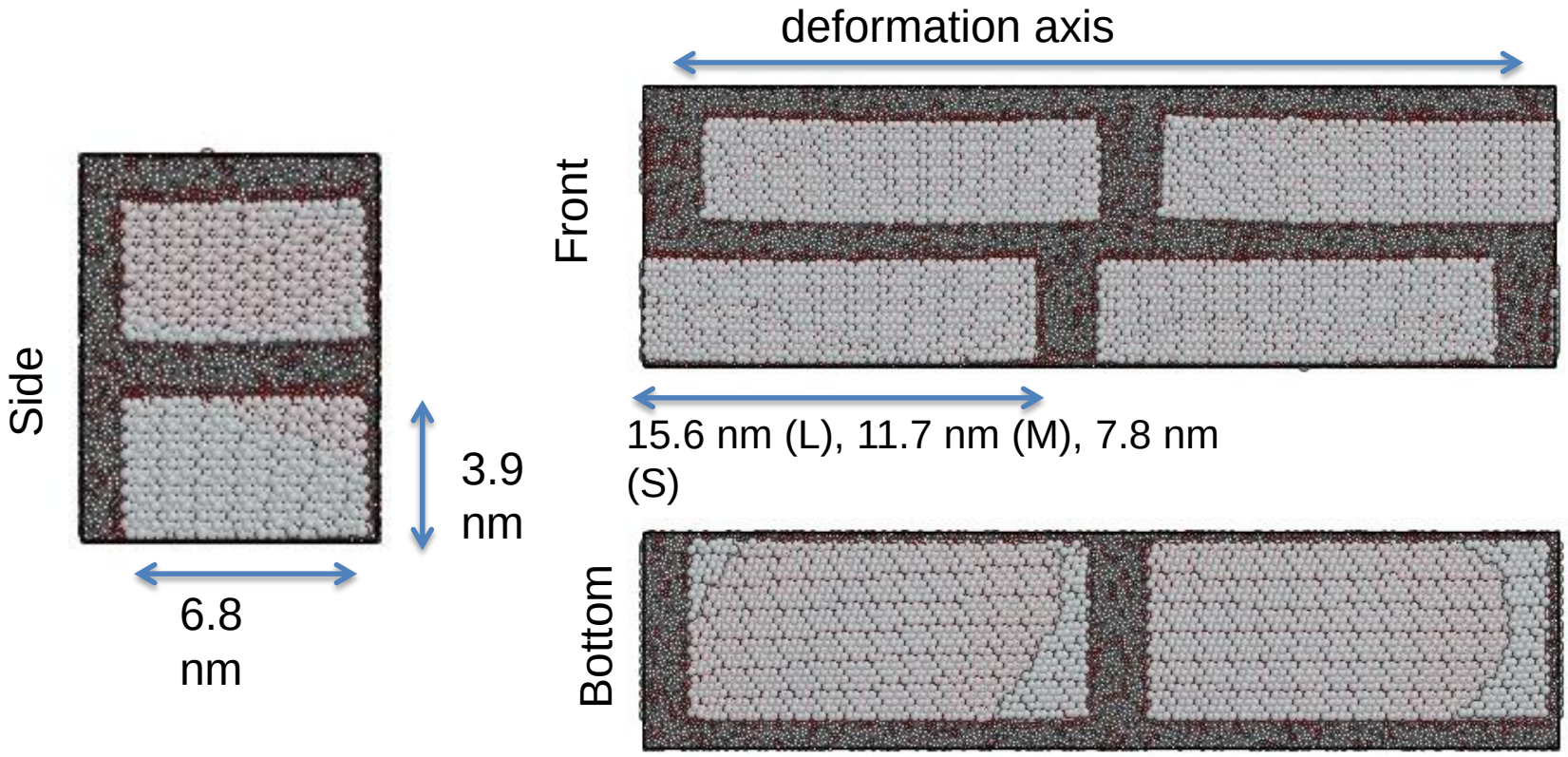
Random tacticity used. Torsion angle between monomer and chain is set to avoid overlaps between polymer atoms in different chains.







System configuration

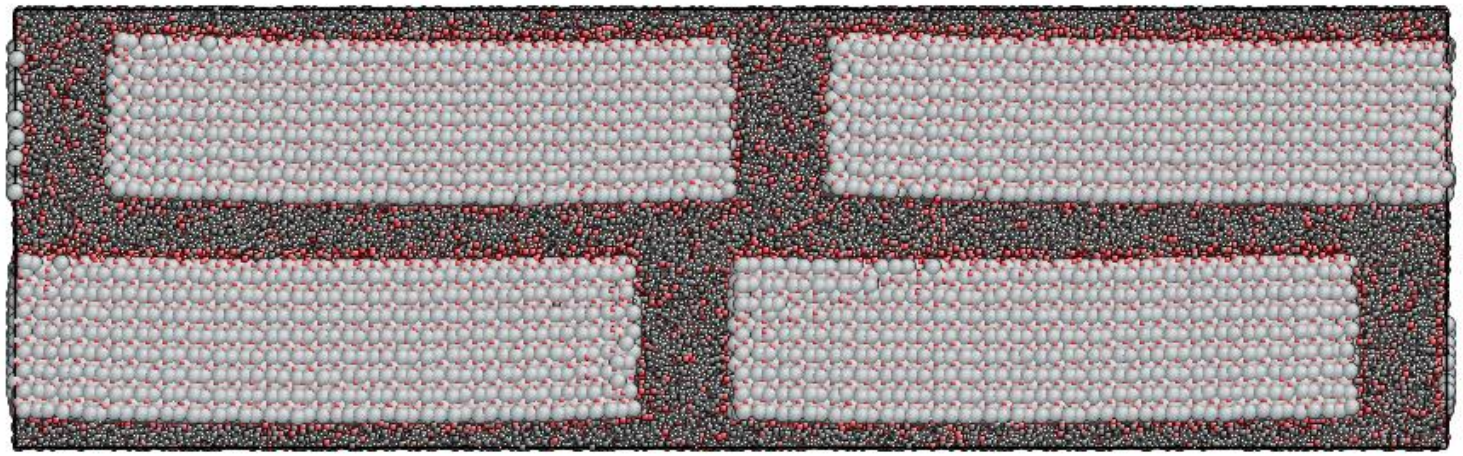


Brick-and-mortar structures built in three different sizes along the direction of the deformation axis with brick dimensions 7.8 nm, 11.7 nm, 15.6 nm for small, medium and large structures, respectively. Other dimensions are same at 6.8 nm and 3.9 nm, respectively. There is a 1.2 nm gap between bricks in all three dimensions. Periodic boundary conditions are applied on three axis. Average PMMA chain length is 50 monomers per chain.

Illustration of loading accommodation in the brick-and-mortar compression test

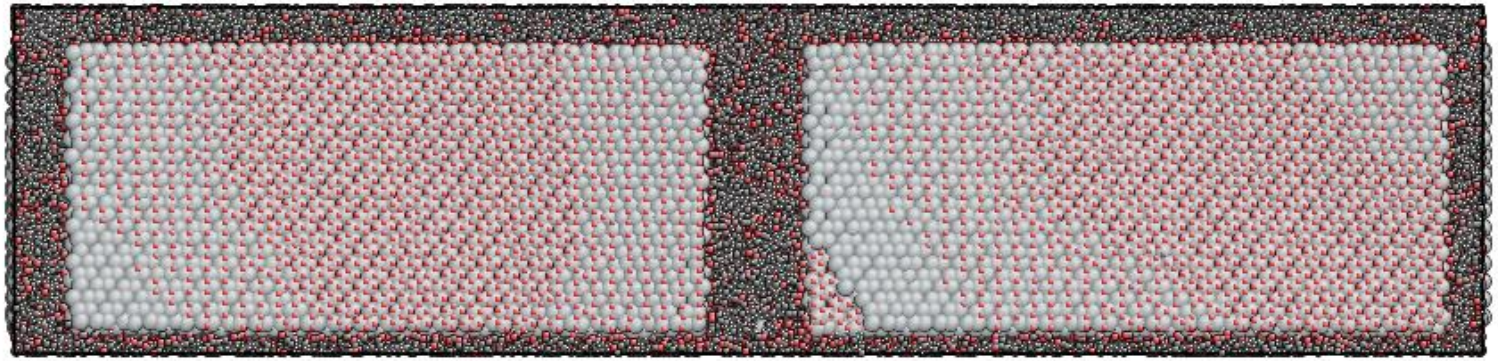
Cross-section Side View

18.4 nm



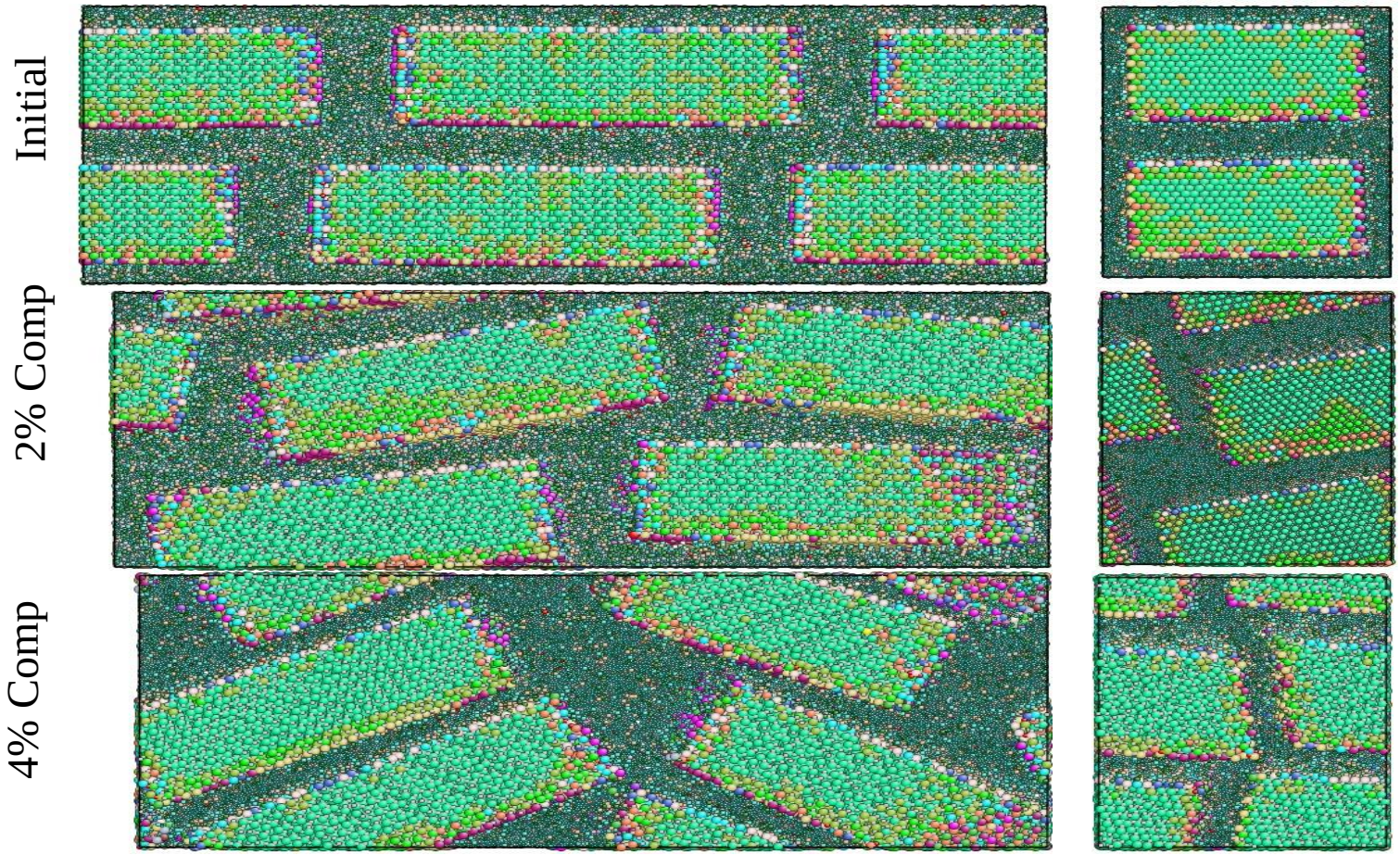
Cross-section Top-Down View

10.4 nm



34.0 nm → 32.9 nm

Illustration of the brick-and-mortar compression test

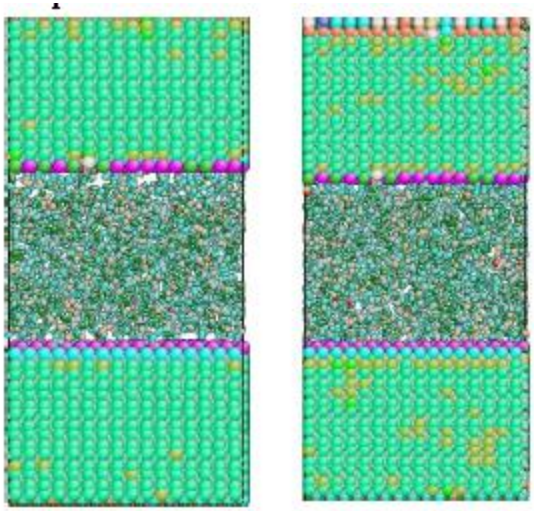


Laminar versus brick-and-mortar structures

System Dimensions:

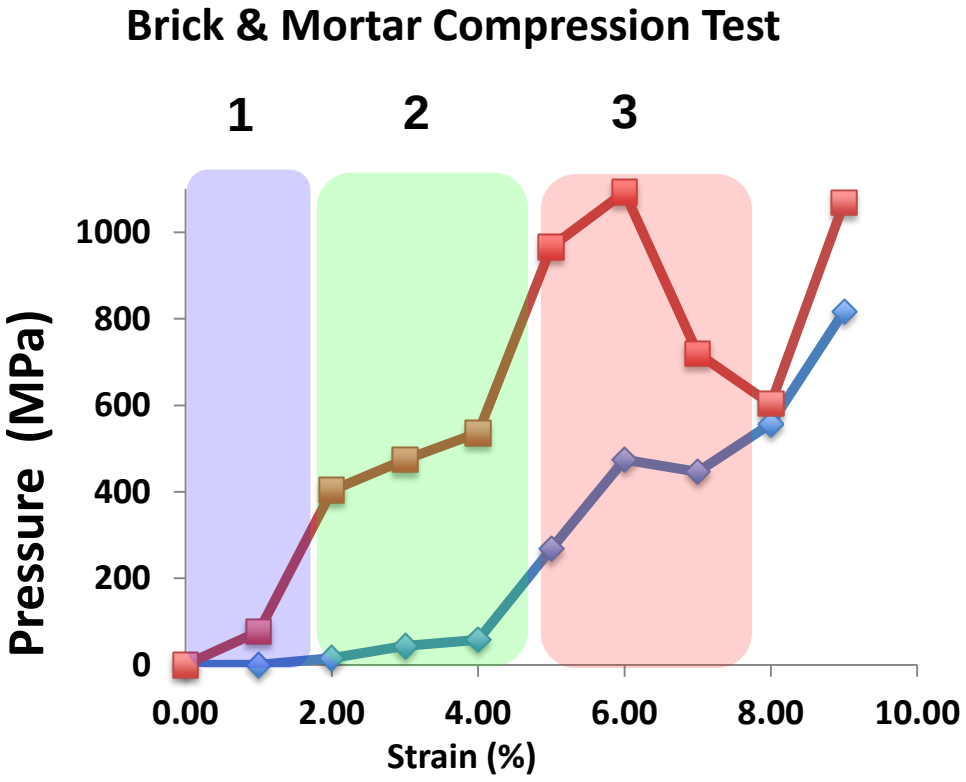
	Brick-and-mortar	Laminar
Small	18.4 x 8.0 x 10.4 (nm)	7.8 x 8.0 x 12.0 (nm)
Medium	26.2 x 8.0 x 10.4 (nm)	11.7 x 8.0 x 12.0 (nm)
Large	34.0 x 8.0 x 10.4 (nm)	15,6 x 8.0 x 12.0 (nm)

1.2 nm gap between bricks, periodic boundary conditions
The average PMMA chain length is 50 monomers per chain
The simulations are performed using the third-generation
Charge Optimized Many-Body (COMB3) potentials

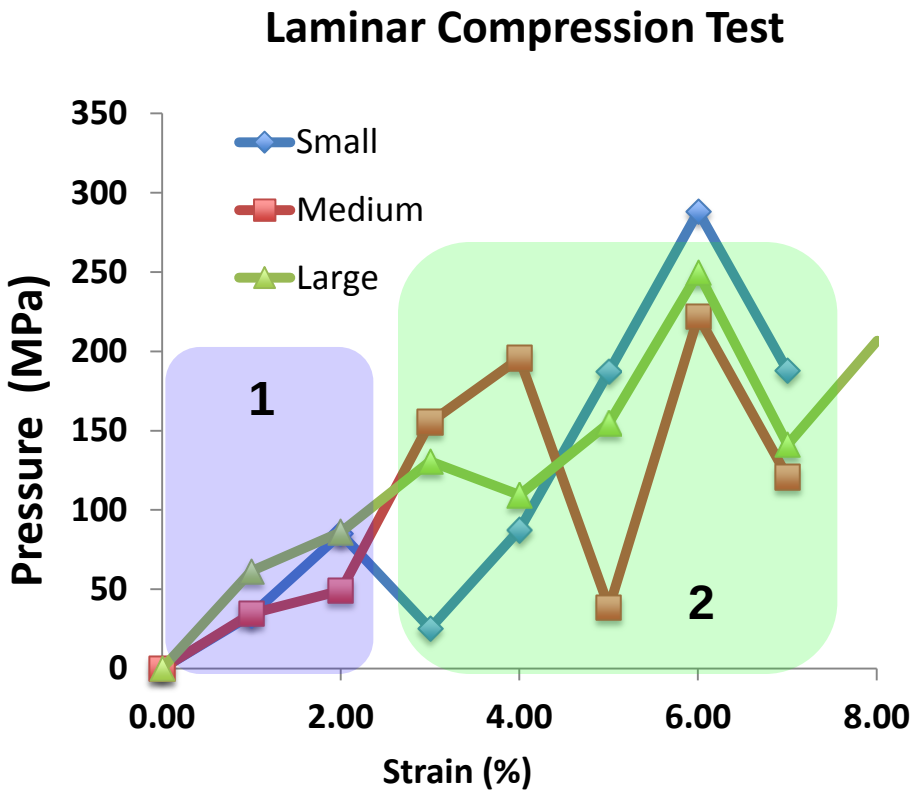


Compression of laminar system

Uniaxial compression test predictions



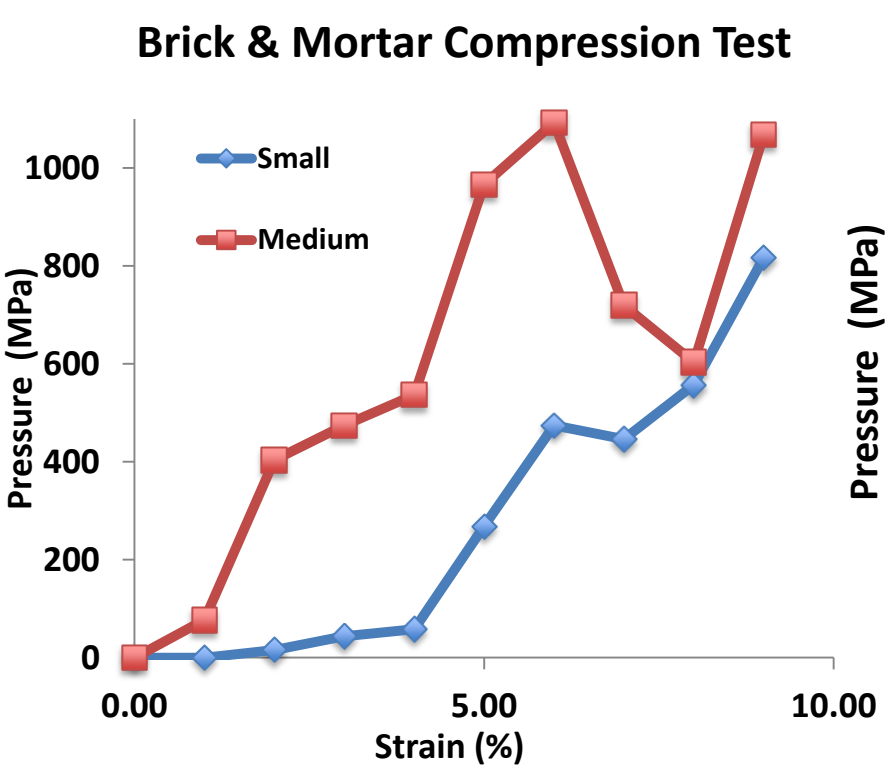
Region 1: Linear region
Region 2: Bricks rotation
Region 3: Two bricks contact

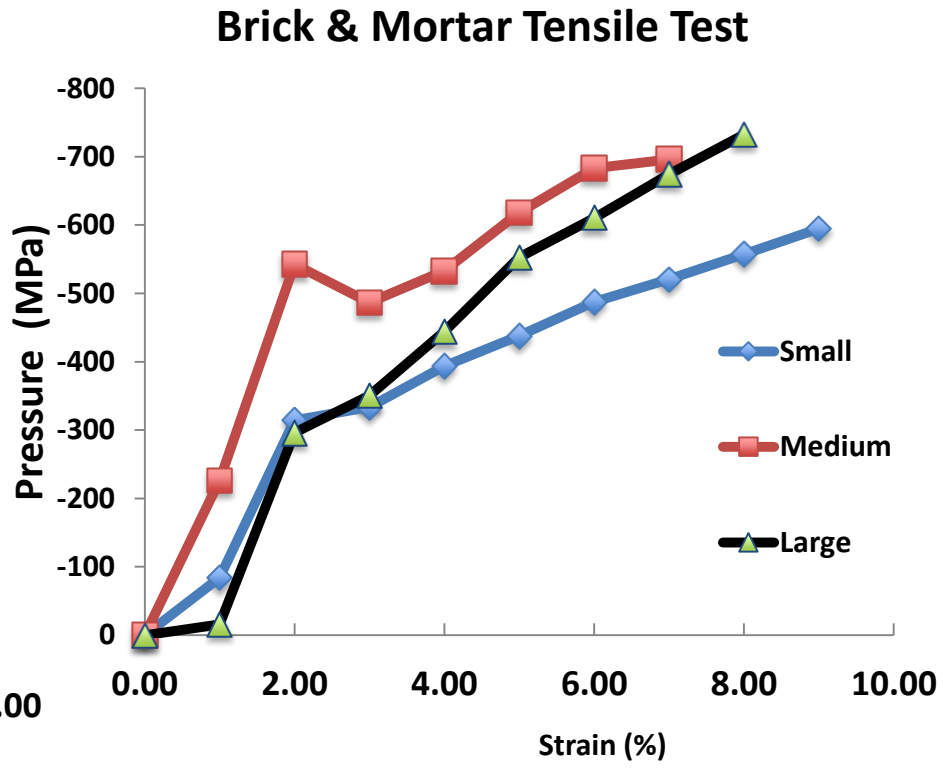


Region 1: Linear region
Region 2: non-linear region

- Mechanisms for brick-and-mortar and laminar composites are quite different
- Brick-and-mortar Young's modulus > laminar Young's modulus
- Elastic properties are dependent on size, especially for brick-and-mortar

Uniaxial compression and tension tests

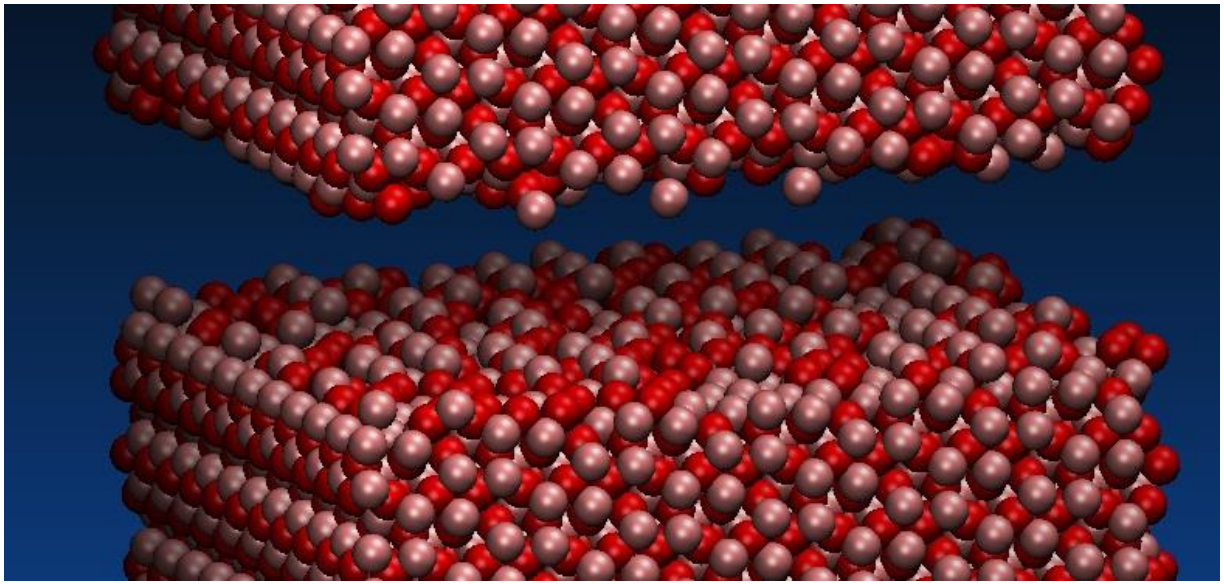




- Pressure along the compression and tension axis given
- Response to tension is more linear than response to compression
- Off-axis motion of bricks results in nonlinear response to the compression

Surface roughness

Surface roughness implemented by randomly deleting surface atoms of the ceramic layers (polymer atoms are not shown)



Large scale molecular dynamics simulations of hybrid materials with smaller fraction of polymer

- Large scale MD simulations of hybrid materials to understand the effect of surface roughness and functionalization to the mechanical properties.
- System size extends to 32.5 nm in x and y axis and 25.7 nm in z axis.
- Polymer/Ceramic ratio is 95%.
- Total number of atoms is ~ 3,000,000.